THE FIRE BEHAVIOUR OF GYPSUM BOARDS INCORPORATING PHASE CHANGE MATERIALS FOR ENERGY STORAGE IN BUILDING APPLICATIONS

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ABSTRACT

In order to study the effect of adding organic phase change materials (PCM) in gypsum board on the latter’s fire performance, thermal analysis and cone calorimetric techniques have been used. The cone calorimeter has been used in both horizontal as well as vertical orientation using spark and pilot ignition sources. For vertical orientation a special sample holder was constructed ‘in house’, which had a frame made of 1.5mm mild steel sheet, without a rear central area but covered with a ceramic board with holes in it to enable easy insertion of thermocouples through them for attaching to the rear surface of the sample. For pilot ignition a simple diffusion butane flame of 50mm length was used. The results were analysed in order to choose one best set of conditions for these sample, which turned out to be vertical orientation with spark igniter on all the time. The rest of samples were tested under these conditions and showed that the ignition and sustainment of the flame in these gypsum boards are dependent on the concentration and distribution of the PCM absorbed in gypsum board. While by an addition method required amount of PCM can be added to the gypsum board, with an immersion method the absorption depends upon the porosity of the material and needs to be engineered to get samples of low flammability.

INTRODUCTION

Thermal energy storage is a key technology for renewable energy utilization and improvement of the energy efficiency of the heating and cooling processes. Solar energy has enormous potential for the heating of buildings in winter, but is time and weather dependent. One way of utilising the solar energy to improve thermal energy storage efficiency of building materials is to use Phase Change Materials (PCMs) in the latter, which are capable of storing a large amount of latent heat during their phase transitions. Heat is absorbed during the daytime and released at night when the material changes from one state to another (e.g. solid to liquid or vice-versa). Organic PCMs such as paraffins, butyl stearate and capric-lauric acids, active as latent heat thermal energy storage materials, have numerous benefits such as no supercooling, chemical stability, low vapour pressure during the phase change and no phase segregation. The selection of the PCM depends on many factors such as: the melting temperature of the PCM must be within the temperature range of operation, the PCM must be chemically stable and should be non toxic, and should not impact overall cost. Paraffin waxes because of these properties and in particular low cost, have been a popular choice so far among various researchers.

PCMs can be incorporated in several forms to building materials like gypsum or concrete. One way is the immersion method, by soaking gypsum blocks into bath of a melted PCM. By optimising the porosity of the gypsum board, the desired amount of PCM can be absorbed. The main disadvantage of this method is that PCM leakage is not avoided. The second method is direct incorporation, where PCMs are added into gypsum during its mixing phase. Since the PCM is uniformly distributed within
the board, the PCM leakage is lower than that by immersion method.

The usage of PCMs, in particular organic, can be detrimental to flammability of the construction materials. The presence of organic PCMs in building materials increases the risks of fire even when incorporated in a non-flammable matrix such as gypsum or cement. Despite a vast amount of literature available on the energy absorbance efficacy of PCMs in the construction materials (gypsum board and concrete), there are only limited studies on the effects of PCMs on flammability of construction materials. As is well known, in recent years, stringent flammability, safety standards and legislations have been imposed on building materials to protect these buildings from fire hazards. In most of the tests the heat release rate of combustibles and ignition time of materials have to be taken into account in order to satisfy the criteria set for making sustainable buildings. The deterministic criteria relate mainly to life safety levels, fire exposure, structural performance, fire growth and spread levels. The aim of this work is to devise a suitable methodology of fire testing them at a micro and laboratory scale, which can be used for screening purpose during material development stage with the potential of passing commercial fire tests at the product development stage in compliance with building codes.

EXPERIMENTAL

Materials

Gypsum powder sourced from British Gypsum, British Gypsum Thistle Multi Finish was used as received. The general composition provided by manufacturer is that it mainly contains calcium sulphate hemihydrate. Other constituents such as clay, limestone (calcium carbonate) and minor amounts of quartz and hydrated lime are also present.

Phase change materials:

- Eutectic mixture (EM), prepared by mixing 30 wt-% dodecanoic (lauric) acid (Acros chemicals) and 70 wt-% decanoic (capric) acid (Acros chemicals)
- Paraffin (Pa) n-octadecane (Alfa Aesar 99%)

Sample preparation

Plaster board was prepared by mixing gypsum powder with water in the ratio of 2.5:1 in order to get a well proportioned slurry. Then, the prepared slurry was poured in a wooden mould of dimensions 122mm x 122mm x 12mm and the mould was placed at room temperature for 7 days to dry. The sample is referred to as Gy in this paper.

PCMs were introduced by two methods, direct incorporation and immersion methods. In direct incorporation method required amount of PCM was added to gypsum powder before making slurry and then poured in a mould to dry for 7 days. These samples are referred to as Gy_PCM_Ad, where Ad stands for additive.

For immersion method two sets of samples were prepared. In the first set the gypsum board samples were immersed in a bath of melted PCM, keeping the temperature slightly above its melting point, for 30 minutes. After that period, samples were removed and dried. The samples were weighed before and after immersion, from which the % PCM absorbed could be determined. This type of samples are referred to as Gy_PCM_Imm (Table 1), where PCM is eutectic mixture (EM) or paraffin (Pa) and Imm stands for immersion. With this ~6.5% (w/w) PCM material could be absorbed in the board. In the second set Gy samples were first placed in a vacuum oven for 10 minutes to draw all the air out of the board. The samples were then immersed in a bath of melted PCM for 30 minutes. With this method upto 22.9% (w/w) PCM could be absorbed (Table 1). These type of samples are referred to as
Gy_PCM_Im_V, where V stands for vacuum. The compositions and densities of all samples are given in Table 1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Method of incorporation of PCM</th>
<th>PCM absorbed/added (wt-%)</th>
<th>Sample thickness (mm)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gy</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>1.70</td>
</tr>
<tr>
<td>Gy_EM_Ad</td>
<td>Addition</td>
<td>10</td>
<td>10</td>
<td>1.22</td>
</tr>
<tr>
<td>Gy_EM_Imm</td>
<td>Immersion</td>
<td>6.5</td>
<td>10</td>
<td>1.50</td>
</tr>
<tr>
<td>Gy_EM_Im_V</td>
<td>Vacuum suction and Immersion</td>
<td>18.3-22.9</td>
<td>10</td>
<td>1.96</td>
</tr>
<tr>
<td>Gy_Pa_Ad</td>
<td>Addition</td>
<td>10</td>
<td>10</td>
<td>1.60</td>
</tr>
<tr>
<td>Gy_Pa_Imm_V</td>
<td>Vacuum suction and Immersion</td>
<td>17.2-18.9</td>
<td>10</td>
<td>1.86</td>
</tr>
</tbody>
</table>

**Thermal analysis**

The thermal behaviour of the PCMs and the gypsum board containing PCMs has been studied by means of an SDT 2960 simultaneous DTA (differential thermal analysis) – TGA instrument from room temperature to 900 °C using 15 ± 1 mg samples heated at a constant rate of 10 °C/min in air flowing at 100 ± 5 mL/min.

**Fire performance**

A cone calorimeter (Fire Testing technology, UK) was used to evaluate the fire performance of gypsum board without / with PCMs. The sample holder and methodology were slightly modified than those described in ISO 5660. The limitation in the quantity of materials available led to the use of specimens of reduced size of 75 mm x 75 mm rather than using the normal 100 mm x 100 mm sizes as outlined in ISO 5660. Previously in our laboratories it was noted that the use of reduced size gave similar relative trends to those observed using 100 mm x 100 mm specimens. Firstly one set of samples containing EM (samples Gy, Gy_EM_Imm and Gy_EM_Ad) was tested according to standard ISO 5660 procedure at 50 and 70 kW/m². No ignition was observed at 50 kW/m², whereas at 70 kW/m² ignition occurred in EM containing samples. Limitation of the cone heater prevented testing above this heat flux.

Cone calorimeter was used in two orientations, horizontal and vertical. Two types of ignition sources, spark and pilot ignition were used and samples tested under different conditions. For pilot ignition a simple diffusion butane flame of 50mm length was provided from a 3.2mm outside diameter stainless steel tube burner arrangement.

Methodology used for two cone orientations is as:

1. Horizontal orientation: A sample holder of 75mm x 75mm dimensions was used as in ISO 5660 with specimens wrapped in the usual way and the height adjusted to 25mm from front face of sample to the cold cone heater face. For pilot ignition, the spark igniter was pushed to the side and the HT cables disconnected; the pilot flame was set, using a retort stand on an adjacent table, the stand was used to hold the pilot flame burner horizontally in a position 10mm above the sample surface with the flame extending from the edge of the sample to slightly beyond the mid-point.
2. Vertical orientation: In this case the cone was moved into vertical orientation and a special sample holder was constructed ‘in house’ from 1.5mm mild steel sheet; 25mm side right angle pieces were folded and cut to the required length and depth and welded up. This yielded a frame without a rear central area with the view that if this was omitted then temperature measurements could be made from the rear face of the sample. The sample holder was provided with an internal backing board of 6mm thick calcium silicate (Duratec 750) followed by a layer of calcium silicate wool immediately behind the sample which was wrapped in the usual way. Further backing boards were cut and drilled for 1mm diameter mineral insulated thermocouples (type 310 stainless steel sheath). Initially a board was marked with a vertical centre line the position of the sample determined and holes for the thermocouple were drilled to match the centre of the sample and points 10mm above and 10mm below the horizontal centre of the sample. This was later replaced with a board marked for the horizontal centre and drilled on the vertical centre of the sample and 10mm each side of that vertical. The thermocouples were pushed through the calcium silicate wool into contact with the sample wrap and then held in place using wire twists. The pilot ignition flame was kept 10mm from the sample face with the orientation as described previously that is a horizontal tube burner with the flame across the sample face approximately 10mm below the horizontal centre line. Because a high irradiance was applied to the sample, a mild steel shutter was constructed with calcium silicate card insulation on the side facing the cone radiator in order to reduce pre-heating of the sample (and the operator). Spark ignition in this case was as in standard orientation. It was found from initial tests that a drip collector was not required for the materials being studied so it was omitted.

A number of tests were performed on one set of samples (gypsum containing EM) with spark igniter on until ignition, spark igniter on all the time, pilot flame on until ignition, and pilot flame on all the time. From this one condition was selected and used for the rest of samples as described in a later section.

RESULTS AND DISCUSSION

Figure 1 shows TGA and DTA curves of the two PCMs used to make composites. Pa starts losing mass at ~105°C, losing 100% mass by 244 °C. EM’s mass loss starts at 130 °C, but the mass loss rate is much higher and by 218 °C all mass is lost. In both cases endothermic peaks can be seen from Figure 1(b) with peak maxima at 193 and 206 °C, respectively, followed by exothermic transitions. The sharp exothermic peak in Paraffin at 232 °C is in good agreement with its auto-ignition temperature of 235 °C, whereas in EM only exothermic base line shift is observed.

The effect of heat on gypsum board is well known from literature. At lower temperatures (100–170 °C) the gypsum loses 75 % of its bound water and is converted from calcium sulfate dihydrate to calcium sulfate hemihydrates. At higher temperatures (130–180 °C) the material loses its remaining bound water and is converted to calcium sulfate anhydrate. From Figure 2a) 16% mass loss is observed between 105 - 180°C. Both endothermic reactions are seen in Figure 2b) as an endothermic peak initiating at 110 °C with maximum at 158 °C. Another reaction occurs around 700 °C. This reaction, seen as 4% mass loss between 650 - 720 °C is believed to be the decarbonation of calcium carbonate. The endothermic peak of the gypsum representing desorption of water and dehydration in both Py_PCM samples is similar to the control (Gy), indicating that PCM presence does not interfere with gypsum’s water release. The exothermic peaks observed for PCMs in Figure 1a) are superimposed by the exothermic base line shift of the gypsum board, indicating that these might not be too much affecting the process. In mass loss curves of PCM containing samples in Figure 2a) the additional mass loss is due to evaporation and combustion of the paraffin and EM.

In conclusion while this study indicates the thermal decomposition behaviour of the two Gy_PCM
materials, there is nothing which suggests that the flammability of the mixture would be increased.

Figure 1. TGA and DTA curves of PCMs

Figure 2. TGA and DTA curves of Gy without / with PCMs incorporated by additive method

Flammability properties

Establishment of cone exposure conditions

One set of samples, gypsum and gypsum containing eutectic mixture (samples Gy, Gy_EM_Ad and Gy_EM_Imm) were tested in horizontal and vertical orientations with spark or pilot igniter on until ignition and igniter on all the time to understand their behaviour in different conditions. All results in terms of time-to-ignition (TTI), peak heat release rate (PHRR), total heat release (THR) and total mass loss during the test are presented in Table 2, while selected HRR and % mass versus time curves are presented in Figures 3 – 5.

The control sample, Gy, did not ignite under any condition. Samples with EM with both immersion and additive methods ignited but the burning (appearance of flame) was very low and erratic, i.e. flame will appear when the EM is exposed to surface irradiance and then disappear and come back again. Samples with immersion method also burnt less vigorously despite expected more PCM on the
surface due to absorption, which can be explained because of low concentration of the PCM in Gy_EM_Imm (~ 6.5% w/w, Table 1). Moreover, since each specimen was individually immersed in the melted EM bath, there was variation in the concentration of EM in different samples, hence there was variation in cone parameters as well.

**Effect of orientation, horizontal versus vertical:** In Figure 3a), the effect of orientation, while the spark igniter was on until ignition, on the cone parameter can be seen. It can be seen that in vertical orientation the PHRR was slightly higher than in the horizontal orientation, the difference though is still within the error range of cone tests. There is no significant effect on the mass loss rate, as seen from Figure 3b).

Figure 3. a) HRR and b) mass loss versus time curves for gypsum boards without/with EM on cone exposure at 70 kW/m² heat flux, horizontal versus vertical orientation with spark ignition till ignition.

**Effect of ignition source, spark versus pilot ignition:** The effect of ignition sources on vertically oriented samples is shown in Figure 4. With the pilot ignition it is difficult to judge when the ignition
has occurred, hence the pilot flame was left on all the time and to compare with spark ignition, the latter was on all the time as well. It should be noted that the heat release observed due to the pilot flame was compensated in the heat release observed by the cone. As can be seen from results, with pilot ignition there was an early ignition than from the spark ignition. PHRR was also increased, but not significantly. THR was not much different. Mass loss rate is also not much affected.

The reproducibility of the test can be seen from Figure 5 where one of the samples has thermocouples on the reverse side. The results are quite consistent, any variations are due to different concentration of PCM in each specimen plus the normal error range of the cone calorimeter (±10%).

Figure 5. a) HRR versus time curves for gypsum boards without/with EM on cone exposure at 70 kW/m² heat flux in vertical orientation with pilot flame ignition all the time for samples without and with thermocouples

Table 2: Cone calorimetric results of gypsum boards without/with EM at 70 kW/m² external heat flux under different orientations and ignition scenarios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Testing condition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>Mass loss (%)</th>
</tr>
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<tbody>
<tr>
<td>Gy</td>
<td>Hor, Spark Ign_STD</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_STD</td>
<td>-</td>
<td>-</td>
<td>9.8</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>Vert, Pilot flame all test</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>Vert, Pilot flame all test</td>
<td>-</td>
<td>-</td>
<td>11.3</td>
<td>16.2</td>
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<tr>
<td>Gy_EM_Ad</td>
<td>Hor, Spark Ign_STD</td>
<td>47</td>
<td>55.3</td>
<td>28.2</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_STD</td>
<td>40</td>
<td>64.6</td>
<td>31.3</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_all test</td>
<td>390</td>
<td>73.2</td>
<td>24.2</td>
<td>22.3</td>
</tr>
<tr>
<td></td>
<td>Vert, Pilot flame all test</td>
<td>45</td>
<td>83.3</td>
<td>33.3</td>
<td>24.1</td>
</tr>
<tr>
<td>Gy_EM_Imm</td>
<td>Hor, Spark Ign_STD</td>
<td>305</td>
<td>61.7</td>
<td>13.6</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_STD</td>
<td>47</td>
<td>95.7</td>
<td>40.2</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_all test</td>
<td>245</td>
<td>67.7</td>
<td>16.2</td>
<td>21.1</td>
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<td></td>
<td>Vert, Pilot flame all test</td>
<td>47</td>
<td>105.5</td>
<td>45.8</td>
<td>23.6</td>
</tr>
</tbody>
</table>
**Effect of igniter: on until ignition or all the time:** There was not much effect of igniter being on all the time or just until ignition as can be seen from results in Table 2.

From these results it can be concluded that in these samples, which are not very flammable, there is not much effect of the orientation, type of igniter and whether it is on all the time or not. In a separate study wood samples were also tested under these conditions to study a flammable material, the results will be published in a forthcoming publication.

**Effect of PCMs on flammability of gypsum board**

Based on above results all the samples were tested in vertical orientation with spark ignition on all the time. Results are presented in Table 3 and Figure 6. As can be seen from results, both samples of Gy_Pa prepared by immersion or direct incorporation method ignited around 23s. Sample from immersion method have much higher PHRR and THR than by direct incorporation method. This is due to higher PCM concentration (22.9%, Table 1) in the former. Sample of Gy_EM prepared by immersion method ignited at 6s, whereas by direct incorporation did not ignite until 162s. As can be seen both types of Gy_EM samples have lower PHRR and THR than respective Gy_Pa sample. Mass loss results are representative of the PCM concentration in the sample. The samples with additives, Gy_EM_Ad and Gy_Pa_Ad have very similar mass loss rates (Figure 6(b)). Mass loss rate is higher for samples made by immersion method due to higher PCM concentration, these being much higher in Gy_EM_Imm sample than Gy_Pa_Imm.

Figure 6 a) HRR and mass loss curves for gypsum boards without/with PCMs on cone exposure at 70 kW/m² heat flux in vertical orientation with flame ignition all the time.
Table 3: Cone calorimetric results of gypsum boards without/with PCMs at 70 kW/m² external heat flux in vertical orientation with flame ignition all the time

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>PHRR (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>Residue (%)</th>
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<tr>
<td>Gy</td>
<td>-</td>
<td>-</td>
<td>2.1±1.33</td>
<td>17.3±1.4</td>
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<tr>
<td>Gy_Pa_Ad</td>
<td>26±18</td>
<td>128±15</td>
<td>41.6±6.3</td>
<td>22.7±0.7</td>
</tr>
<tr>
<td>Gy_Pa_Imm_V</td>
<td>23±8</td>
<td>537±69</td>
<td>133.1±30</td>
<td>29.7±0.7</td>
</tr>
<tr>
<td>Gy_EM_Ad</td>
<td>162±18</td>
<td>82±11</td>
<td>311±4.9</td>
<td>25.7±3.9</td>
</tr>
<tr>
<td>Gy_EM_Imm_V</td>
<td>6±2</td>
<td>490±49</td>
<td>101.8±9.6</td>
<td>30.5±3</td>
</tr>
</tbody>
</table>

*Out of three samples, one contained thermocouples attached to the unexposed surface.

The thermocouples embedded on the reverse sides of the sample enabled the measurement of temperature of the unexposed surface as a function of time during the test. As an example results of Gy, Gy_Pa_Ad and Gy_Pa_Imm_V are shown in Figure 7. Trends in rise of temperatures in different types of samples are reflection of heat release rate versus time curves. Gy, which does not burn, has a low temperature rise until 470 s, probably due to loss of water after which voids may be created within the sample, hence coherence is lost and the temperature starts rising, reaching 480 °C after 1000s. Gy_Pa_Ad behaves very similarly to Gy until ~550s despite ignition at 26s, which can be explained due to the reason that ignition occurred on the surface and the burning was very low, but after 550s, the temperature rose more than the Gy, reaching 570 °C after 1000s. However, in Gy_Pa_Imm sample, due to much higher Pa concentration there was an early ignition and burning was persistent, the temperature rise is much higher from 33s onwards, reaching maximum 600 °C after 960s. These results will be used to validate the heat transfer modelling work being carried out in our laboratories.

Figure 7. Temperature versus time curves of the reverse surfaces of gypsum and gypsum containing paraffin samples on cone exposure at 70 kW/m² heat flux in vertical orientation with pilot igniter on all the time.
CONCLUSIONS

This work has shown that while required amount of PCM can be added to the gypsum board, with immersion method the absorption depends upon the porosity of the material. By subjecting the sample to vacuum prior to inserting in the molten PCM bath, the air could be extracted and hence porosity increased. The flammability of the materials tested by a vertically oriented sample holder in a vertically oriented cone and using a spark ignition throughout the test showed that the gypsum board does not ignite. Organic PCM such as paraffin and eutectic mixture when present in gypsum board ignite, but the burning is dependent on the concentration as well as dispersion of the PCM. If the PCM is in low concentration, the sample ignites, the flame goes out and then ignites again. However, with immersion method, due to higher concentration of the PCM on the surface of the sample, the ignition was early, flame was persistent and with high peak heat release rate. The measured temperature profiles of samples during the course of the tests give useful insight into the behaviours of the heat exposed samples.

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